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PATENT SPECIFICATION

NO DRAWINGS

Inventors: RAYMOND FREDERICK HILTON, ROBERT JOSEPH JULIETTI and
KEVIN TERRY BRACEY-WRIGHT

L119,180



L119,180

Date of filing Complete Specification: 22 Nov., 1967.

Application Date: 1 April, 1966.

No. 14694/66.

Complete Specification Published: 10 July, 1968.

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Index at acceptance: —D1 P(AX, B2B1, B3, C1B, C1H2B, C1H2D, C1H2X, C1H3A, C1H3B, C1H3D, C1H3X, C2B3, C2C2, C2C3); B1 E3B1; B2 E(1A, 1H); D1 R3

Int. Cl.: —D 06 m 11/00

COMPLETE SPECIFICATION

Forming Deposits within Porous Material

ERRATUM

SPECIFICATION No. 1,119,180

Page 1, Heading, Date of filing Complete
Specification: for "22 Nov., 1967" read
"22 March, 1967"

THE PATENT OFFICE
2nd January 1969

corresponding oxide or to other compounds.

It is known to form coatings of certain metal oxides by depositing the hydroxide of the metal concerned on a surface, and heating this to convert it to the corresponding oxide. Such a process is not applicable however, to forming deposits of hydroxide on interior surfaces of porous material, since the metal hydroxide first coats the outside of the material, and access to within it is thereby prevented.

According to the present invention a process for forming deposits of metal hydroxides on interior surfaces of porous material comprises:

- (1) contacting, without precipitation of hydroxide, the interior surfaces with (a) an aqueous solution of at least one metal salt from which the corresponding hydroxide may be precipitated at a pH between 1.7 and 12.5 and (b) a substance capable of decomposing at the pH of the solution to give ammonia with a consequent rise of the pH, and
- (2) initiating decomposition of the said sub-

[Prior

among the types of porous material to which the process of the present invention may usefully be applied are fibrous material, such as ceramic fibre blankets and woven cotton, and also sponges and porous brick.

The process of the invention may be carried out using the aqueous solution of any metal salt of which the corresponding hydroxide precipitates from a salt solution of sufficient concentration on raising the pH to a value between 1.7 and 12.5. Suitable metallic cations include copper, silver, beryllium, magnesium, calcium, zinc, cadmium, mercury (mercurous), yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, zirconium, thorium, tin (stannous), lead, chromium (chromic), uranium, manganese, iron (ferrous and ferric), cobalt, nickel, ruthenium, rhodium, palladium and iridium. Salts of aluminium, iron, chromium and manganese have been found particularly suitable. Mixtures of salts can also be used. Where it is desired to form an aluminium hydroxide deposit aluminium oxychloride has been found to be a particularly suitable salt, as the

SEE ERRATA SLIP ATTACHED

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Int. Cl.: —D 06 m 11/00

COMPLETE SPECIFICATION

Forming Deposits within Porous Material

We, MORGANITE RESEARCH AND DEVELOPMENT LIMITED, a company organised under the laws of Great Britain, of Battersea Church Road, London S.W.11., do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to forming deposits within porous materials. In particular, the invention is concerned with the deposition on the interior surfaces of a porous material of a metal hydroxide which hydroxide may subsequently be reduced, or converted to the corresponding oxide or to other compounds.

It is known to form coatings of certain metal oxides by depositing the hydroxide of the metal concerned on a surface, and heating this to convert it to the corresponding oxide. Such a process is not applicable however, to forming deposits of hydroxide on interior surfaces of porous material, since the metal hydroxide first coats the outside of the material, and access to within it is thereby prevented.

According to the present invention a process for forming deposits of metal hydroxides on interior surfaces of porous material comprises:

- (1) contacting, without precipitation of hydroxide, the interior surfaces with (a) an aqueous solution of at least one metal salt from which the corresponding hydroxide may be precipitated at a pH between 1.7 and 12.5 and (b) a substance capable of decomposing at the pH of the solution to give ammonia with a consequent rise of the pH, and
- (2) initiating decomposition of the said sub-

stance, thereby raising the pH of the solution to a value such that the corresponding hydroxide of the metal is precipitated and a deposit thereof formed on the said interior surfaces.

Preferably these steps are followed by heating the material containing precipitated hydroxide to convert the latter to the corresponding oxide or, in appropriate circumstances, described below, to a water-insoluble salt of the metal.

In this way a comparatively even distribution of metal oxide or salt within the porous material can be obtained.

Among the types of porous material to which the process of the present invention may usefully be applied are fibrous material, such as ceramic fibre blankets and woven cotton, and also sponges and porous brick.

The process of the invention may be carried out using the aqueous solution of any metal salt of which the corresponding hydroxide precipitates from a salt solution of sufficient concentration on raising the pH to a value between 1.7 and 12.5. Suitable metallic cations include copper, silver, beryllium, magnesium, calcium, zinc, cadmium, mercury (mercurous), yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, zirconium, thorium, tin (stannous), lead, chromium (chromic), uranium, manganese, iron (ferrous and ferric), cobalt, nickel, ruthenium, rhodium, palladium and iridium. Salts of aluminium, iron, chromium and manganese have been found particularly suitable. Mixtures of salts can also be used. Where it is desired to form an aluminium hydroxide deposit aluminium oxychloride has been found to be a particularly suitable salt, as the

{Prior

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ensuing ammonium chloride sublimes off from the product on heating.

5 The anion of the metal salt is preferably chosen such that no noxious fumes are produced during the drying or any other subsequent heating step.

10 As the substance capable of decomposing under the process conditions of the invention to give ammonia, hexamethylene tetramine has been found to be particularly suitable, this decomposing at 90°C in the presence of water, to give ammonia and provide the necessary increase in pH of the salt solution. An alternative suitable substance is urea which likewise decomposes on heating to give ammonia. To obtain a more rapid production of ammonia the urea may be admixed with a catalyst such as urease. Ammonia is produced from such a mixture in effective amounts by warming to 40°C. Salts of urea, such as urea orthophosphate, $[\text{CO}(\text{NH}_2)_2]_3\text{H}_3\text{PO}_4$, may also be used to advance, where the acid moiety of the urea salt is derived from an acid forming a water-insoluble salt with the metal cations of the metal salt. The acid which is freed on decomposition of the urea salt can thus react with the precipitated metal hydroxide to convert it to an insoluble salt. Heating may be necessary to effect this conversion satisfactorily.

25 Other compounds which may be found suitable include condensation products of aldehydes and ammonia. As will be apparent from the above, a wide variety of materials are available for the process of the present invention, and it is important, in determining whether they are suitable, merely that they should be capable of decomposing at the pH of the aqueous solution to give ammonia, thereby raising the pH of the aqueous solution containing them. It will thus be evident, for example, that materials such as aliphatic and aromatic amines are unsuitable, since these only decompose under alkaline conditions and in a manner tending to lower the pH.

30 The concentration of the aqueous solution of the metal salt, its pH, and the amount of the substance capable of decomposing to give ammonia are all inter-related. The concentration of the metal salt will be dependent on the amount of the final hydroxide or oxide that is required as a deposit on the interior surfaces of the material. The concentration will also depend on the absorption capability of the porous substrate material, and will inevitably be limited by the solubility of the salt chosen at the temperature employed. It will thus be apparent that the solubility of the salt must be at least such as to enable sufficient hydroxide to be precipitated to form an adequate deposit.

35 The pH to which the aqueous solution of the metal salt is brought depends primarily on the pH at which the corresponding metal

hydroxide is precipitated, but it also depends in part on the concentration of the salt in that solution. Thus a pH of 4 is the highest value at which a useful amount of aluminium salts can be kept in aqueous solution, but lower values of pH may be required to maintain high concentrations of aluminium in solution. As an example, it may be mentioned that a 5% solution of aluminium oxychloride will be stable up to a pH of 3.5, the hydroxide being precipitated at higher values of pH, whereas a 25% solution of the aluminium oxychloride will precipitate hydroxide if the pH is raised above 3.0.

40 The amount of ammonia producing substance to be employed is dependent upon the change in pH it is desired to bring about by liberation of ammonia. The ammonia is required, firstly to neutralise any free acid present and, secondly to raise the pH of the solution to a value where quantitative precipitation of hydroxide occurs. When forming an aluminium hydroxide deposit, it has been found that as the pH is raised from the point where hydroxide precipitation begins, precipitation is qualitative. When a pH of about 7 is reached, quantitative precipitation takes place. Consequently the amount of ammonia producing substance used will depend upon the extent to which the solution has been acidified and on the amount of ammonia required to cause quantitative aluminium hydroxide precipitation. It has, however, been found that in usual practice a slight excess of the ammonia producing substance over the theoretical quantity necessary to produce a desired change in pH is desirable, as the metal salt may, to some extent, act as a buffer, and any such effect must be overcome if substantially complete precipitation of the metal hydroxide is to be obtained. Large excess of ammonia in the process is to be avoided however, as this can cause the precipitated aluminium hydroxide to re-dissolve.

45 In carrying out the present invention, it is normally most convenient to form a mixture in aqueous solution of the metal salt and the ammonia producing substance and then to adjust the pH of the mixed solution to the desired value. Where deposition over all the interior surfaces is required, the porous material is then immersed in this pH adjusted solution. Where a deposit is required on only a part of the interior surfaces, then a different method may be employed, for example, spraying the pH adjusted mixed solution on to one side of the porous material, followed by heating to precipitate the hydroxide.

50 Before initiating decomposition of the ammonia producing substance excess liquid is normally removed from the porous material to avoid both waste and unwanted precipitation of the hydroxide. After removing excess liquid, the process conditions are altered so that ammonia is liberated from the ammonia

producing substance. This is normally achieved by heating, though where urea is employed, ammonia could be obtained by a subsequent addition of urease or other decomposition catalyst. The extent to which any heating of the porous material is necessary will of course depend on the particular ammonia producing substance being employed, but where urea alone, or hexamethylene tetramine, are used, heating to at least 90°C., preferably at least 100°C., is required, and where a urea/urease mixture is used, warming to 40°C is normally sufficient.

Following the production of ammonia and, with the consequent rise in pH, precipitation of the metal hydroxide, the surplus water is removed by drying e.g. at a temperature of 100°C to 200°C. If an oxide deposit is required or a deposit of a salt of the metal, as may be obtained when urea orthophosphate is used, the temperature is raised substantially after drying e.g. to at least 300°C., so as to convert the metal hydroxide to the corresponding oxide or salt. It should be understood that as this heating normally takes place in air, there may be some change in valency state of the metal in converting the hydroxide to the oxide or salt. The term "corresponding oxide" is thus intended to encompass all oxides and mixtures thereof that may be obtained by heating the metal hydroxide.

This heating step has the further effect of burning off any residues of organic material remaining from the ammonia producing substance, and leaving a deposit of substantially pure metal oxide on the interior surfaces of the porous material.

As stated above, this invention is applicable to the forming of deposits on the interior surfaces of porous materials generally, and in particular on the interior surfaces of fibrous materials such as ceramic fibre blankets, woven cotton, and also sponges and porous bricks. The deposits may be formed throughout the thickness of the material or they may be restricted to a part thereof, which could for example simply be a thin layer adjacent one surface. It is envisaged that the invention will be found to be of particular value in forming deposits on ceramic fibres made up into a blanket. Ceramic fibre blankets find a special application as insulating material, particularly at very high temperatures, as heat losses account for a very large part of the operating cost of high temperature processes. Ordinary ceramic fibre blankets are not, however, rigid and self-supporting, and thus their application to heated apparatus is relatively difficult. By the process of the present invention, a ceramic fibre blanket may be obtained with a deposit of a metal oxide, such as aluminium oxide, on the interior surfaces, this making the blanket quite sufficiently rigid to be self-supporting. It is believed that this rigidity is obtained through the metal

hydroxide being deposited as discrete nodules around the fibres and especially at points of intersection of two or more fibres thus locking them together.

Applying the process of the invention to carbonaceous materials, such as woven cotton and sponges, enables a final product to be obtained consisting substantially entirely of highly porous metal oxide or water-insoluble salt, since at the temperatures employed in converting the metal hydroxide to the corresponding oxide or to a salt of the metal all carbonaceous matter, including the original cotton or sponge substrate, may be burned away. Such porous material can be of value as a catalyst in chemical reactions.

Examples of the process of this invention will now be given.

EXAMPLE 1

A solution of hexamethylene tetramine is made up with a concentration of 30 grams of solute per 100 ml. of water. Concentrated hydrochloric acid is added to reduce the pH from about 8 to 4. The volume of solution is measured and an equal volume of aluminium oxychloride solution is added.

The aluminium oxychloride is material EX. 5025 as supplied by R & D Polymers Ltd. which contains 11.5 wt. % of aluminium (combined). The pH of the mixture is rechecked to ensure that it is between 3 and 4.

A "Triton" (Trade Mark) blanket of ceramic fibres is immersed in the mixed solution, and complete impregnation is ensured by gentle squeezing. It is found that 8.8 ml. of solution is required per cubic inch of blanket.

The wet impregnated blanket is then removed from the mixed solution placed in an oven and heated to a temperature of from 100° to 200°C. The heating decomposes the hexamethylene tetramine, releasing ammonia which causes a rise in the pH of the solution entrapped within the fibres of the blanket, causing precipitation of aluminium hydroxide on the interior surfaces of the blanket. This heating is maintained so that at the same time as the ammonia is liberated the water is gradually driven off, resulting after approximately 3 hours in substantially dry material.

The blanket is now in a usable form as a stiffened material. It is brownish in colour due to carbonaceous residue from the hexamethylene tetramine.

Generally the process is continued with a step of heating the blanket to approximately 800°C. At this temperature the aluminium hydroxide is converted to the corresponding oxide, Al_2O_3 , and at the same time the carbonaceous residue from the hexamethylene tetramine is burned out.

EXAMPLE 2

30 grams of urea are dissolved in 100 ml.

of water. An equal volume of aluminium oxychloride solution is added and a "Triton" blanket (as in Example 1) is impregnated with the mixture. The wet blanket is placed in an oven and heated with a steadily rising temperature from ambient temperature to 400°C. in 2 hours. The blanket is stiffened in the range 300—400°C and it keeps its clean white colour. It is not brown as when hexamethylene tetramine is used and therefore it does not need to be cleaned by firing in an oxidising atmosphere to burn off carbonaceous residues. Subsequent heating to 800°C converts the hydroxide to aluminium oxide.

15 EXAMPLE 3

16.5 parts by weight of aluminium chloride hydrate are dissolved in 55.7 parts by weight of water, and 27.8 parts by weight urea orthophosphate, $[\text{CO}(\text{NH}_2)_2]_3\text{H}_3\text{PO}_4$, are slowly added to the solution. The resulting solution is painted or sprayed on to the surface of a "Triton" blanket so as to penetrate a small distance. The blanket is then heated to 400°C and a rigid surface structure is obtained. It is thought that fine aluminium hydroxide is formed which then combines with the phosphoric acid to form a rigid coating. This coating is resistant to attack by molten mill scale which is present in steel reheat furnace applications where fibre blanket is used for insulation purposes. In this particular case only a surface stiffening is required but the whole blanket could of course be treated with the urea orthophosphate solution, if so desired.

35 WHAT WE CLAIM IS:—

1. A process for forming deposits of metal hydroxides on interior surfaces of porous material comprising:

- 40 (1) contacting without precipitation of hydroxide, the interior surfaces with (a) an aqueous solution of at least one metal salt from which the corresponding hydroxide may be precipitated at a pH between 1.7 and 12.5 and (b) a substance
- 45 capable of decomposing at the pH of the solution to give ammonia with a consequent rise of the pH, and
- 50 (2) initiating decomposition of the said substance, thereby raising the pH of the solution to a value such that the corresponding hydroxide of the metal is precipitated on the said interior surfaces.

2. A process according to claim 1 wherein the metal salt is a salt of aluminium, iron, chromium or manganese.

3. A process according to claim 2 wherein the metal salt is aluminium oxychloride.

4. A process according to any preceding claim wherein the said substance capable of

decomposing to give ammonia is or includes 60 hexamethylene tetramine or urea.

5. A process according to claim 4 wherein the said substance is urea admixed with urease as a catalyst.

6. A process according to any one of claims 1 to 3 wherein the said substance capable of decomposing to give ammonia is a salt of urea, the acid moiety of the urea salt being derived from an acid forming a water-insoluble salt with the metal cations of said metal salt. 70

7. A process according to claim 6 wherein the urea salt is urea orthophosphate.

8. A process according to any preceding claim wherein the material is subsequently heated whereby the precipitated hydroxide is converted to the corresponding oxide or to a water-insoluble salt of the metal. 75

9. A process according to claim 8 wherein the material is heated to at least 300°C.

10. A process according to any preceding claim wherein the porous material is a fibrous material, sponge or porous brick. 80

11. A process according to claim 10 wherein the fibrous material is ceramic fibre blanket. 85

12. A process according to claim 10 wherein the fibrous material is woven cotton.

13. A process for forming deposits on interior surfaces of porous material substantially as described in either Example 1 or 2. 90

14. A process for forming deposits on interior surfaces of porous material substantially as described in Example 3.

15. A porous material having a deposit formed on interior surfaces thereof whenever prepared by a process according to any preceding claim. 95

16. A porous material according to claim 15 wherein the deposit is formed substantially throughout the material. 100

17. A porous material consisting substantially entirely of at least one metal oxide and/or of a water soluble salt prepared by forming a deposit on the interior surfaces of a substrate water-insoluble salt prepared by forming a deposit on the interior surfaces of a substrate consisting of porous carbonaceous material by means of a process according to any one of claims 1 to 10 and 12, and subsequently burning away the said substrate at a temperature at least sufficient to convert precipitated metal hydroxide to the corresponding oxide or to a water-insoluble salt of the metal. 110

For the Applicants,
CARPMAELS & RANSFORD,
Chartered Patent Agents,
24 Southampton Buildings,
Chancery Lane, London, W.C.2.

Axtell, Carol (CA)

From: Nilsen, Kevin (KJ)
Sent: Friday, June 02, 2006 10:40 AM
To: Axtell, Carol (CA)
Subject: FW: CONFIDENTIAL INFORMATION ON CTI'S SiC DPF
Information Classification: DOW RESTRICTED - For internal use only

Carol,

Please start a JF with the Title, "CTI-SiC DPFs" including this E-mail. Will give you paper copy of the translated license.

Thanks

Kevin

-----Original Message-----

From: Nilsen, Kevin (KJ)
Sent: Friday, May 05, 2006 3:04 PM
To: Krier, Kurt (KK)
Cc: Lawrey, Gary (G)
Subject: RE: CONFIDENTIAL INFORMATION ON CTI'S SiC DPF

Kurt,

Asked for translation by 5/10, but may be a bit after that. Partially my fault, your E-mail got a little buried.

Regards

Kevin

-----Original Message-----

From: Krier, Kurt (KK)
Sent: Tuesday, May 02, 2006 9:44 AM
To: Nilsen, Kevin (KJ)
Cc: Lawrey, Gary (G)
Subject: FW: CONFIDENTIAL INFORMATION ON CTI'S SiC DPF
Importance: High

Kevin, we had a discussion with CTI this morning. They are are very interested in pursuing the discussion further. We asked for a copy of the license between Faurecia and CTI and they have provided it. We also asked for the patent. Can you review both to understand if there are any issues we need to be aware of. Our area interest is also on freedom of practice and also if there are any prior relationships that would restrict our potential sales activity. The license is in French so we may need to get it interpreted.

Kurt Krier

Dow Automotive

Office Phone: (248) 829-2952

Fax: (248) 391-6393

6/2/2006

-----Original Message-----

From: nadine delbianco [mailto:nadine.delbianco@ctisa.fr]

Sent: Tuesday, May 02, 2006 9:02 AM

To: Krier, Kurt (KK)

Subject: CONFIDENTIAL INFORMATION ON CTI'S SIC DPF

Dear Kurt,

According to our conversation, please find in the annexed file the licence signed on March 2005 by Faurecia-IFP-CTI.

Don't hesitate to ask us complementary informations.

The American reference of our patent (common patent with the French Institute of Petrole) is US 6 582 796 B1 date of patent june 24 2003.

Title is "Monolithic honeycomb structure made of porous ceramic and use as particulate filter".

About our plugging patent for the moment, I have only the French one so I will send it to you by post. We will send to you also the economical informations as promised.

Staying at your disposal,
With all our best regards

Nadine DELBIANCO
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